Environmental Pollution 180 (2013) 165–172

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Co-contaminants and factors affecting the sorption behaviour of two sulfonamides in pasture soils

Prakash Srinivasan [a,b], Ajit K. Sarmah [c,*], Merilyn Manley-Harris [b]

[a] Landcare Research New Zealand, Private Bag 3127, Hamilton, New Zealand
[b] Chemistry Department, University of Waikato, Private Bag 3105, Hamilton, New Zealand
[c] Department of Civil & Environmental Engineering, Faculty of Engineering, The University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

ARTICLE INFO

Article history:
Received 22 February 2013
Received in revised form
7 May 2013
Accepted 7 May 2013

Keywords:
Veterinary antibiotics
Steroid hormones
Pasture soil
Sorption
pH-Partitioning

ABSTRACT

We investigated the effect of soil pH, organic carbon, ionic strength and steroid hormones on the sorption of sulfamethoxazole (SMO) and sulfachloropyridazine (SCP) in three pastoral soils of New Zealand. A model linking sorbate speciation with species-specific sorption coefficients describing the pH dependence of the apparent sorption coefficients was used to derive the fraction of each species of SMO. All soils displayed a decrease in sorption when pH was increased, with SMO exhibiting the highest sorption at pH 2. The cationic form of SMO appeared to sorb more close to pH $\geq$ pK_{a1} and, when pH $\geq$ pK_{a2} (6.5, 7.5 and 8.5) the anionic species seems to dominate, however, its sorption affinity to all soils was low. SMO sorption was affected by ionic strengths and organic carbon content, while the presence of hormones showed only a subtle decrease in SCP sorption in a selected model pasture soil.

1. Introduction

Unlike many overseas countries, New Zealand (NZ) raises its large population of ruminant animals on pasture with the exception of the intensively housed fed poultry and pig industries, where antibiotics are used in feed (Sarmah et al., 2006). The NZ dairy industry is also a significant consumer of antibiotics, with intramammary and injectable forms dominating. Overall veterinary antibiotics usage in the NZ animal industry amounts to about 55 tonnes per year, of which agricultural operations consume nearly 13 tonnes of penicillins, 11 tonnes of sulfonamides (SAs) and macrolides annually; while another 25 tonnes of bacitracin are used by the poultry industry (Ministry of Agriculture and Forestry, 2010). After administration, up to 80% of antibiotics can be excreted in the urine and faeces of the animals posing a potential ecological and health risk to the environment (Halling-Sørensen, 1998; Tolls, 2001). Given that land-application of animal waste effluent is a permitted activity in NZ, and coupled with the direct excretal input from the millions of grazing livestock, there is potential risk of antibiotic residues entering the environment. Long term exposure to low concentrations of these antibiotics could be toxic to non-target terrestrial and aquatic organisms (Kummerer, 2003). Similar risk from antibiotics due to grazing animals, or confined animal feeding operations which are widely practiced in the USA, Canada, China, Australia and many other countries in the Europe, could also occur. Thus understanding the fate of these compounds in soils is a first logical step to develop effluent management practices and to mitigate their ecological health risks.

To date, most soil sorption studies within the sulfonamide group were focussed on sulfadiazine (Sukul et al., 2008), sulfamethazine (Figueroa-Diva et al., 2010; Kurwadkar et al., 2007; Lertpaitoonpan et al., 2009; Thiele-Bruhn and Aust, 2004); sulfachloropyridazine (ter Laak et al., 2006); sulfathiazole (Kahle and Stamm, 2007a; Kurwadkar et al., 2007); sulfadimethoxine, sulfaguanidine (Bialk-Bielinska et al., 2012) and sulfapyridine (Schwarz et al., 2012). These studies have shown that sorption of these compounds to soils is generally low and is a function of sorbent properties. They undergo pH-dependent speciation, and can become charged or uncharged species and thus affecting their sorption affinity to soils. Previously reported partition coefficients (K_d) of sulfonamide antibiotics were found to vary with texture and soil properties (Boxall et al., 2002; Kahle and Stamm, 2007a; Kurwadkar et al., 2007; Thiele-Bruhn and Aust, 2004), albeit with contrasting K_d values. For instance, Boxall et al. (2002) reported a decrease in K_d for SCP, whereas Sukul et al. (2008) found a significant increase in sorption of sulfadiazine, with manure addition in soils. Determination of environmental fate of SA's is often difficult due to the inconsistency encountered in relation to their mobility as it is dependent on the

* Corresponding author.
E-mail address: a.sarmah@auckland.ac.nz (A.K. Sarmah).

0269-7491/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envpol.2013.05.022

sorbents and the associated experimental conditions and soil factors (Bialk-Bielinska et al., 2012). No published information is currently available on the soil sorption of SMO, an important antibiotic within the group.

Veterinary antibiotics are likely to co-occur with other antibiotics or contaminants, including pesticides, hormones and fertilisers (Kolpin et al., 2002; Monteiro and Boxall, 2009), which can lead to ecotoxicity on terrestrial and aquatic organisms. Only a few published studies are available in the literature on the potential interactions between veterinary antibiotics and other contaminants, emphasizing the persistence and bioavailability aspect (Accinelli et al., 2006; Chun et al., 2005), however, the effect of steroid estrogens on the overall sorption behaviour of sulfonamides in soil has been hitherto neglected. Steroid hormones such as 17β-estradiol (E2), and its primary metabolite estrone (E1) are naturally excreted in the faeces and urine of dairy cows and other livestock. Thus, agricultural antibiotics and natural estrogens, and the associated metabolites are likely to occur in a pasture environment simultaneously and may influence the compounds fate in soils. No studies have so far been attempted to elucidate the role of hormones on the sorption of sulfonamide antibiotics in pasture soils. Therefore the main aim of this study was to investigate the effect of pH, ionic strength and organic carbon content on the sorption capacity of SMO to selected NZ pasture soils. A secondary objective was to determine the sorption of SCP in the presence of a natural steroid hormone, E2 in a model pastoral soil collected from a dairy farming region in the North Island of NZ.

2. Materials and methods

2.1. Chemicals

SMO, SCP, 17β-Estradiol (>98% purity), estrone (>99% purity) (SI-Table 1), and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$ >99% purity) were obtained from Sigma Aldrich, Australia. Acetonitrile (Mallinckrodt ChromAR, ≥99.8% purity), dichloromethane (Mallinckrodt UltimAR, ≥99.9% purity), methanol (Mallinckrodt ChromAR, ≥99.9% purity), concentrated hydrochloric acid (HCl) and potassium hydroxide (KOH) were obtained from Biolab Scientific Ltd. New Zealand. High Performance Liquid Chromatography (HPLC) grade deionised water was obtained from an onsite Arium® 61316 high performance reverse osmosis system (Sartorius Stedim Biotech GmbH, Germany).

2.2. Soils

Four topsoils (0–5 cm) with contrasting organic carbon (OC) content, fine earth particle size distribution, pH, and cation exchange capacity (CEC) were selected (Table 1). Of the four soils, three soils (Te Kowhai silt loam, Hamilton clay loam, and Horotiu silt loam) were from the Waikato dairy farming areas, while Matawhero silt loam was from the Gisborne region of the North Island of NZ. The soils were collected fresh, air dried, sieved (<2 mm), and stored at 4 °C before use. A full description of the soils and the methods used to determine their physico-chemical properties can be found elsewhere (Blakemore et al., 1987).

2.3. Batch sorption studies

Stock solutions of each target compound (SMO and SCP) at a concentration of 1000 mg L^{-1} were prepared by dissolving appropriate amounts of each active ingredient in methanol. Six initial aqueous solution concentrations ranging from 1.5, 3, 5, 7.5, 10 and 15 mg L^{-1} for SMO and 0.75, 1.75, 2.75, 4, 5.5 and 7.5 mg L^{-1} for SCP were prepared in duplicates in 0.005 M $CaCl_2$ solution. Experimental protocol involved constructing batch sorption isotherms separately by adjusting pH and ionic strength, and spiking steroid hormone 17β-estradiol (E2) of two known concentrations in the presence of SCP antibiotic in a selected model soil (Hamilton clay loam). SCP was chosen in preference to the SMO antibiotic as the former seemed to exhibit higher sorption affinity to soils than SMO in a preliminary trial (Srinivasan et al., 2010).

2.4. Adjustment of pH and ionic strength

For the first part of the experiment KOH and HCL were used to adjust pH to the target values of 2, 3, 4, 5.5, 6.5, 7.5, and 8.5. To account for the neutralizing capacity of soils the pH of the aqueous solution was measured before and after equilibration. The mediator solution was prepared by adding an appropriate amount of $CaCl_2 \cdot 2H_2O$ to deionised water to obtain three different concentrations (0.005, 0.05 and 0.2 M), which corresponded to 0.01, 0.1, 0.4 M in ionic strength for cations. The ionic strength was calculated using the following equation.

$$I = \frac{1}{2}\sum_{i=0}^{n} m_i v_i^2 \quad (1)$$

where, I is the ionic strength (mg L^{-1}); m_i concentration of the ith ion (mg L^{-1}) and v_i, is the charge of the ith ion. The mediator solutions were later used to prepare six different aqueous concentrations of the SMO.

For the second part of the experiment, appropriate amounts of $CaCl_2$ were dissolved in deionised water to obtain 0.005 M, 0.05 M and 0.2 M $CaCl_2$ solution and the six initial aqueous solution concentrations were prepared using them as mediator solution at soil pH. To investigate the co-contaminant effect on the sorption of SCP antibiotic in a model soil, six initial aqueous concentrations of SCP in 0.005 M $CaCl_2$ were prepared in duplicates. An appropriate amount of E2 stock solution was spiked into tubes containing six different SCP concentrations to yield of 0.075 and 3 mg L^{-1} of E2 respectively.

Batch studies were performed following a protocol similar to Sarmah et al. (2008). Briefly, duplicate samples of air-dried soils (2 g) were weighed into glass centrifuge tubes (35 mL) with Teflon-lined screw caps. Aliquots (30 mL) of six concentrations of SMO were added to the respective tubes, wrapped in aluminium foil, placed in the dark to limit photo-degradation and shaken in an end-over-end shaker for 24 h. Preliminary kinetic studies showed that 24 h of contact time was sufficient to attain equilibrium (Srinivasan et al., 2010). Solutions containing only the antibiotic but without soil (soil blank), and solution containing only soil in 0.005 M $CaCl_2$ without antibiotic (antibiotic blank) served as controls. It was ascertained that there was no significant sorption loss of SMO, SCP and E2 to the glassware. These treatments were included in all experiments to determine container sorption losses and to check for interfering peaks including the analysis of mobile phase.

2.5. HPLC/UV analysis

Following centrifugation and filtration, samples of SMO and SCP were analysed using a C_{18} Luna column. An isocratic mobile phase of acetonitrile: trifluoroacetic acid (0.05%): tetrahydrofuran in a ratio of 40:55:5 for SMO and 32:63:5 for SCP (v/v) at 1.0 mL min^{-1} and an injection volume of 20 μL was used. The limits of detection (LOD) were calculated on a signal to noise ratio of 3 to 1. LOD for SMO and SCP was 0.02 μg mL^{-1} using the UV detector, and was improved to 0.005 μg mL^{-1} (SMO) by using a fluorescence detector (excitation and emission wavelength were 272 and 340 nm respectively) in tandem with UV detection. The limits of quantification (LOQ) for SMO and SCP were ~13 μg kg^{-1}. A full description of the analytical method used can be found in Srinivasan et al. (2012). Spiked steroid hormone, 17β-estradiol (E2) and estrone (E1) from soil samples were also analysed using HPLC and UV detection following a complex solvent extraction step as detailed in Sarmah et al. (2010). A brief description is given in supplementary information in Appendix A.

2.6. Data analysis and sorption modelling

Sorption isotherms were modelled using the Freundlich model: $C_s = K_f C_w^N$, where C_s (μg g^{-1}) and C_w (μg mL^{-1}) are the equilibrium sorbed and aqueous phase concentrations respectively, K_f (μg^{1-N} mL^N g^{-1}) is the Freundlich sorption coefficient and N (dimensionless) is the measure of sorption non-linearity ($N = 1$ represents a linear isotherm). Due to observed inconsistency in isotherm linearity for the majority of soil–solute combinations, it was difficult to compare K_d or K_{oc} values between solutes or soils as they were concentration-dependent. Thus, in order to compare sorption across soils, a concentration-dependent effective distribution coefficient ($K_d^{eff} = K_f C_w^{N-1}$) was calculated with an equilibrium concentration of 0.5 mg L^{-1} (Table 2).

Table 1
Selected properties of soils used in the study.

Soils	pH 1:2 H_2O	pH 1:2.5 $CaCl_2$	OC (%)	CEC ($cmol_c$ kg^{-1})	Sand %	Silt %	Clay %	SSA[a] (m^2g^{-1})
Matawhero silt loam	6.1	4.3	2.1	15.4	11	62	27	6.0
Te Kowhai silt loam	6.7	5.1	5.0	22.3	9	54	37	32.5
Horotiu silt loam	5.7	5.4	8.2	35.6	34	48	17	16.1
Hamilton clay	5.8	4.8	4.0	21.5	19	51	30	36.0

[a] Specific surface area was measured by para nitro-phenol adsorption (Hedley et al., 2000).